Refinement

Refinement on F
$R = 0.048$
$wR = 0.068$
$S = 1.829$
1259 reflections
164 parameters
H atoms fixed
$w = 4F_o^2/[\sigma^2(F_o^2) + 0.0036F_o^4]$
$(\Delta/\sigma)_{\max} = 0.019$
$\Delta\rho_{\max} = 0.14$ e Å^{-3}
$\Delta\rho_{\min} = -0.13$ e Å^{-3}
Extinction correction: isotropic (Zachariasen, 1963)
Extinction coefficient: 0.25×10^{-5}
Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

Table 1. *Selected geometric parameters (Å, °)*

N2—N3	1.300 (4)	N7—C6	1.459 (3)
N2—N7	1.345 (3)	N7—C8	1.352 (4)
N3—N4	1.354 (4)	C1—C6	1.536 (3)
N4—C8	1.301 (4)	C8—C9	1.484 (5)
N3—N2—N7	106.1 (2)	C6—C1—C12	116.8 (2)
N2—N3—N4	111.0 (2)	N7—C6—C1	111.7 (2)
N3—N4—C8	106.1 (3)	N7—C6—C5	108.7 (2)
N2—N7—C6	122.0 (2)	C1—C6—C5	112.3 (2)
N2—N7—C8	107.9 (2)	N4—C8—N7	108.9 (3)
C6—N7—C8	130.1 (2)	N4—C8—C9	127.8 (3)
C2—C1—C6	109.3 (2)	N7—C8—C9	123.2 (3)
C2—C1—C12	110.3 (2)		

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *CAD*-4 *Software*. Data reduction: *SDP* (Frenz, 1985). Program(s) used to solve structure: *MULTAN*80 (Main *et al.*, 1980). Program(s) used to refine structure: *SDP*. Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *CIF VAX* in *MolEN* (Fair, 1990).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: CF1161). Services for accessing these data are described at the back of the journal.

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2-(2-Bromo-4,5-dimethoxyphenyl)-2-(dimethylamino)acetonitrile

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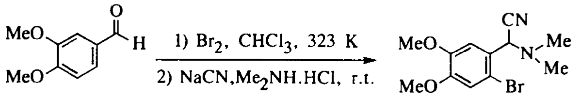
Abstract

The regioselective synthesis, spectrometric data (^{1}H and ^{13}C NMR, and MS) and the X-ray crystal structure determination of the title compound, $C_{12}H_{15}BrN_2O_2$, are reported. In spite of the presence of a Br atom *ortho* to the bulky α-aminonitrile group, normal molecular dimensions have been found.

Comment

The title compound is a member of the α-aminonitrile family of derivatives, which are useful building blocks for the development of new synthetic methods in the field of α-amino acids (Davis, Portonovo, Reddy & Chiu, 1996), aminoamides (Taillades, Rossi, Garrel, Marull & Commeyras, 1996), thiadiazoles (Weinstock, Davis, Handelsman & Tull, 1967), imidazole derivatives (Matier, Owens & Comer, 1973) and oxazoles (Verschave, Vekemans & Hoornaert, 1984). In the course of the present investigations directed towards the preparation of a series of polyhalogenated deoxybenzoins, the α-aminonitrile (II) was synthesized.



(I) (II)

Taking into account that only the crystal structure determinations of a couple of aliphatic α-aminonitriles of type (II) have been reported (Parfonry, Tinant, Declercq & Van Meerssche, 1986; Parfonry, Declercq, Tinant & Van Meerssche, 1988), the X-ray structure of the title brominated aromatic α-aminonitrile, (II), was determined in order to expand the structural knowledge of this synthon.

Within experimental limits, the aromatic ring is essentially planar, with the methoxy groups at C6 and C7 slightly displaced out of the ring plane [deviations of 0.185 (5) and 0.115 (5) Å for C10 and C9, respectively].

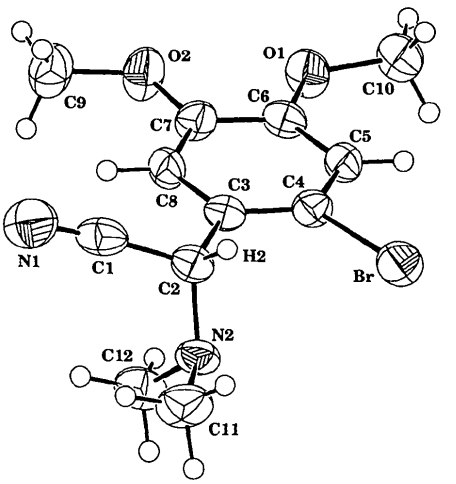


Fig. 1. The molecular structure of (II) with the numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. H atoms are represented as spheres of arbitrary radii.

Despite the different nature and size of the substituents at C2, the chiral center is hardly distorted from the tetrahedral angle, with bond angles N2—C2—H2 and N2—C2—C1 of 108 (2) and 111.1 (4)°, respectively. Besides, the nitrile moiety shows only a small deviation from linearity with an N1—C1—C2 angle of 173.9 (6)°. This behaviour is similar to that displayed by compounds exhibiting an analogous combination of amino and nitrile functionalities, such as hexahydropyrido-2*H*,6*H*-pyrido-[2,1-*b*][1,3,4]oxadiazine-6-carbonitriles (Chiaroni *et al.*, 1993).

On the other hand, the dimethylamino group is rotated out of the ring plane with a dihedral angle N2—C2—C3—C4 of 72.2 (6)°, which could be attributed to an eventual steric hindrance due to the Br substituent at the C4 position. Compared with other bromo-containing aromatic rings (Berger & Bolte, 1994; Kokila, Puttaraja, Kulkarni & Shivaprakash, 1996), the bond angles around C4 show slight variations. This behaviour might be the result of the lengthening of the Br—C4 bond distance due to the presence of the *ortho* α-aminonitrile substituent. A similar behaviour is also observed around C6 and C7 probably due to the *o*-dimethoxy substituents.

Experimental

Reagents and starting materials were obtained from Aldrich Co. and Probus S. A. (Barcelona, Spain) and used without further purification. Operating under an argon atmosphere, a solution of Br_2 (99%, 3.9 ml, 76.1 mmol) in $CHCl_3$ (5 ml) was added dropwise to a stirred solution of 3,4-dimethoxybenzaldehyde, (I) (99%, 13 g, 77.5 mmol), in $CHCl_3$ (104 ml) at room temperature, and the reaction mixture stirred at 323 K for 16 h. Once concentrated under pressure, the crude product was washed with $CHCl_3$ and evaporated *in vacuo* on a rotary evaporator. Crystallization of the solid material obtained from MeOH afforded 2-bromo-4,5-dimethoxybenzaldehyde, (II) (17.100 g, 90%). This compound was dissolved in acetonitrile (342 ml) by gentle heating and added very slowly to a solution of NaCN (98%, 5.816 g, 115.8 mmol) and NH_2Me_2Cl (99%, 15.859 g, 192.7 mmol) in H_2O (114 ml) at room temperature. Stirring was continued at the same temperature overnight. The crude product was concentrated *in vacuo* to eliminate acetonitrile and diluted with H_2O (~100 ml). The aqueous layer was extracted with Et_2O (4 × 50 ml). The combined ether phases were washed successively with H_2O (3 × 20 ml), saturated sodium disulfite (5 × 20 ml) and brine (3 × 20 ml) and dried over anhydrous magnesium sulfate. The solvent was removed by evaporation *in vacuo* at 323 K (bath temperature). The obtained yellow oil was crystallized from MeOH yielding the title compound as a white powder (19.2 g, 89%) (m.p. 345–346 K). Spectroscopic data of the title compound on a Bruker AC250: ^1H NMR: 2.33 (6H, *s*, 2 × NMe), 3.86 (3H, *s*, OMe), 3.89 (3H, *s*, OMe), 4.95 (1H, *s*, H-2), 7.04 (2H, *s*, H-5 and H-8). ^{13}C NMR: 41.6 (2 × NMe), 56.2 (2 × OMe), 62.2 (C-2), 112.4, 116.1 (C-5 and C-8), 104.7, 114.9, 115.1 (C-1,C-3 and C-4), 148.1, 148.9 (C-6 and C-7). MS *m/z*: 298 (M^+, 8), 300 (M^+, 9), 257 (13), 255 (13), 254 (100), 176 (16), 132 (27), 117 (8), 102 (11), 83 (36).

Crystal data

$C_{12}H_{15}BrN_2O_2$
$M_r = 299.17$
Monoclinic
$P2_1/n$
$a = 8.025\ (1)$ Å
$b = 19.844\ (3)$ Å
$c = 8.370\ (1)$ Å
$\beta = 97.44\ (1)°$
$V = 1321.7\ (3)$ Å^3
$Z = 4$
$D_x = 1.503$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71070$ Å
Cell parameters from 25 reflections
$\theta = 7$–$12°$
$\mu = 3.103$ mm^{-1}
$T = 293\ (2)$ K
Prism
0.25 × 0.23 × 0.20 mm
Colourless

Data collection

Enraf–Nonius CAD-4 diffractometer
ω–2θ scans
Absorption correction: refined from ΔF^2 (*XABS2*; Parkin, Moezzi & Hope, 1995)
$T_{min} = 0.448$, $T_{max} = 0.538$
3854 measured reflections
3854 independent reflections

1456 reflections with $I > 2\sigma(I)$
$\theta_{max} = 30.02°$
$h = -11 \rightarrow 11$
$k = 0 \rightarrow 27$
$l = 0 \rightarrow 11$
3 standard reflections
frequency: 120 min
intensity decay: 3%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.029$
$wR(F^2) = 0.116$
$S = 0.852$
2164 reflections
163 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.0547P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} = -0.001$
$\Delta\rho_{max} = 0.225$ e Å^{-3}
$\Delta\rho_{min} = -0.238$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

Br—C4	1.911 (4)	C1—C2	1.487 (7)
O1—C6	1.353 (4)	C2—C3	1.511 (6)
O1—C10	1.433 (5)	C3—C4	1.368 (6)
O2—C7	1.361 (5)	C3—C8	1.395 (6)
O2—C9	1.431 (5)	C4—C5	1.388 (5)
N1—C1	1.133 (6)	C5—C6	1.378 (6)
N2—C12	1.443 (5)	C6—C7	1.384 (6)
N2—C2	1.454 (6)	C7—C8	1.378 (5)
N2—C11	1.459 (5)		
C6—O1—C10	116.8 (4)	C3—C4—C5	122.7 (4)
C7—O2—C9	117.5 (4)	C3—C4—Br	121.2 (3)
C12—N2—C2	112.8 (4)	C5—C4—Br	116.1 (4)
C12—N2—C11	111.4 (4)	C6—C5—C4	119.5 (4)
C2—N2—C11	111.9 (4)	O1—C6—C5	124.4 (4)
N1—C1—C2	173.9 (6)	O1—C6—C7	116.3 (4)
N2—C2—C1	111.1 (4)	C5—C6—C7	119.3 (4)
N2—C2—C3	112.7 (4)	O2—C7—C8	125.0 (4)
C1—C2—C3	111.8 (4)	O2—C7—C6	115.1 (4)
C4—C3—C8	116.7 (4)	C8—C7—C6	119.9 (4)
C4—C3—C2	121.9 (4)	C7—C8—C3	121.9 (4)
C8—C3—C2	121.4 (4)		

An absorption correction by integration from crystal form was performed, but results were not satisfactory, probably due to the uncertainty in the indexing of the crystal faces. Owing to crystal loss, we were forced to use the *XABS*2 procedure (Parkin, Moezzi & Hope, 1995). The H atoms were apparent in the difference map but they were included in the refinement as riding atoms in calculated positions with two common isotropic displacement parameters. The only exception was the H2 atom, for which the positional parameters were refined.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *CAD*-4 *Software*. Data reduction: *Xtal*3.2 (Hall, Flack & Stewart, 1992). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *PLATON*94 (Spek, 1994*a*) and *PLUTON*94 (Spek, 1994*b*). Software used to prepare material for publication: *SHELXL*93.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: AB1437). Services for accessing these data are described at the back of the journal.

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2-[2-(Hydroxyethyl)phenoxy]benzoic Acid

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Abstract

The three-dimensional structure of the title compound, $C_{15}H_{14}O_4$, has been determined. The molecule assumes a skew conformation, the angle between the two phenyl rings being 84.8 (1)°. The carboxylic acid substituent is essentially coplanar with the ring. The molecules are connected by O···O intermolecular hydrogen bonds ranging from 2.6 to 2.9 Å. Distorted bond angles at the substituted phenyl C atoms were observed and they agree with the values reported in the literature for other bridged diphenyls.

Comment

The present work is part of a long-term project concerned with the synthesis of artificial receptors for antiviral compounds. The molecule under investigation, (I), is an intermediate compound for the synthesis of an artificial receptor with a xanthonic nucleus. The com-

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